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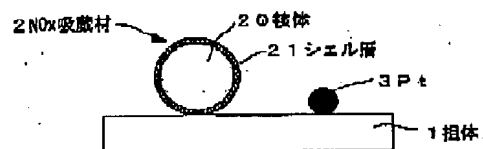
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(54) 【発明の名称】 排ガス浄化用触媒

(57) 【要約】

【課題】 アルカリ金属の移動を抑制し、NO_x 浄化能の耐久性を高める。【解決手段】 NO_x 吸蔵材は、アルカリ金属からなる核体と核体の周囲を覆うシェル層とからなるコア・シェル構造をもち、シェル層はアルカリ土類金属、希土類元素、Mn、Fe、Co、及びNiから選ばれる元素を含む。高温時にはシェル層が固体状態であるので、アルカリ金属の移動がシェル層によって規制される。

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【特許請求の範囲】

【請求項1】 酸化物担体に少なくともアルカリ金属を含む NO_x 吸蔵材と貴金属とを担持してなる NO_x 吸蔵還元型の排ガス浄化用触媒であって、

該 NO_x 吸蔵材は、アルカリ金属からなる核体と該核体の周囲を覆うシェル層とからなるコア・シェル構造をもち、該シェル層はアルカリ土類金属、希土類元素、Mn、Fe、Co、及びNiから選ばれる元素を含むことを特徴とする排ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、酸素過剰のリーン雰囲気中 NO_x を吸蔵し、還元成分過剰のリッチ雰囲気中吸蔵された NO_x を放出して還元できる NO_x 吸蔵還元型の排ガス浄化用触媒に関する。

【0002】

【従来の技術】近年、二酸化炭素による地球温暖化現象が問題となり、二酸化炭素の排出量を低減することが課題となっている。自動車においても排ガス中の二酸化炭素量の低減が課題となり、燃料を酸素過剰雰囲気中で希薄燃焼させるリーンバーンエンジンが開発されている。このリーンバーンエンジンによれば燃料の使用量が低減されるため、二酸化炭素の排出量を抑制することができる。

【0003】このリーンバーンエンジンにおいて、常時は酸素過剰の燃料リーン条件で燃焼させ、間欠的に燃料ストイキ〜リッチ条件とすることにより排ガスを還元雰囲気として NO_x を還元浄化するシステムが開発され、実用化されている。そしてこのシステムに最適な触媒として、リーン雰囲気中 NO_x を吸蔵し、吸蔵された NO_x をストイキ又はリッチ雰囲気中放出する NO_x 吸蔵材を用いた NO_x 吸蔵還元型の排ガス浄化用触媒が開発されている。

【0004】例えば特開平5-317652号公報には、Baなどのアルカリ土類金属とPtを $\gamma\text{-Al}_2\text{O}_3$ などの多孔質酸化物担体に担持した排ガス浄化用触媒が提案されている。また特開平6-31139号公報には、Kなどのアルカリ金属とPtを $\gamma\text{-Al}_2\text{O}_3$ などの多孔質酸化物担体に担持した排ガス浄化用触媒が提案されている。さらに特開平5-168360号公報には、Laなどの希土類元素とPtを $\gamma\text{-Al}_2\text{O}_3$ などの多孔質酸化物担体に担持した排ガス浄化用触媒が提案されている。アルカリ金属、アルカリ土類金属及び希土類元素は NO_x を吸蔵放出する特性を有しているため、 NO_x 吸蔵材と称されている。

【0005】この NO_x 吸蔵還元型触媒を用いれば、空燃比をリーン側からバルス状にストイキ又はリッチ側となるように制御することにより、排ガスもリーン雰囲気からバルス状にストイキ又はリッチ雰囲気となる。したがって、リーン側では NO_x が NO_x 吸蔵材に吸蔵され、それがストイキ又はリッチ側で放出されてHCやCOなどの還元性成分と反応して浄化されるため、リーンバーンエンジ

ンからの排ガスであっても NO_x を効率よく浄化することができる。また排ガス中のHC及びCOは、貴金属により酸化されるとともに NO_x の還元にも消費されるので、HC及びCOも効率よく浄化される。

【0006】 NO_x 吸蔵還元型触媒では、酸素過剰のリーン雰囲気において排ガス中のNiが貴金属の触媒作用で酸化されて NO_2 となり、それが水蒸気によって亜硝酸イオンあるいは硝酸イオンとなって NO_x 吸蔵材と反応して吸蔵される。したがって貴金属と NO_x 吸蔵材とは互いに近接して担持されていることが望ましく、これによって NO_x 吸蔵能が最大に発現され高い NO_x 浄化率が実現される。

【0007】一方、 NO_x 吸蔵材としてのアルカリ金属は、高温域における NO_x 吸蔵能に欠けているため、近年の高温の排ガス中で用いられる NO_x 吸蔵還元型触媒には必須成分となっている。したがって NO_x 吸蔵還元型触媒には、貴金属とアルカリ金属とが必須であり、しかも互いに近接して担持されていることが望ましい。

【0008】ところがアルカリ金属は一般に融点が低く、高温時に担体上を移動して貴金属表面を覆い、これによって貴金属の活性が低下して NO_x 吸蔵能が低下するという不具合があった。例えばカリウムは、 K_2O の状態では融点が402℃であり、 NO_x を吸蔵した $\text{K}(\text{NO}_3)$ の状態では融点が337℃となる。そのため400℃程度の排ガス温度で液化化し、担体上を流動して貴金属を覆ってしまう。

【0009】そこで貴金属とアルカリ金属をそれぞれ別の担体粒子に分離して担持したり、担体層で分離したりすることが行われているが、近接して担持する場合に比べて NO_x 吸蔵能が低下し NO_x 浄化率も低下するという問題がある。また、高温時に飛散するアルカリ金属や、多孔質酸化物担体あるいはコーゼライトなどの基材に固溶するアルカリ金属もあり、このようになると NO_x 吸蔵能が低下して、貴金属の活性低下と同様に NO_x 浄化率が低下してしまう。

【0010】したがって最も望ましいのは、高温時におけるアルカリ金属の移動を防止することであるが、アルカリ金属自身の特性という事情から、有効な対策は見出されていないのが現状である。

【0011】

【発明が解決しようとする課題】本発明はこのような事情に鑑みてなされたものであり、アルカリ金属の移動を抑制し、 NO_x 浄化能の耐久性を高めた触媒とすることを目的とする。

【0012】

【課題を解決するための手段】上記課題を解決する本発明の排ガス浄化用触媒の特徴は、酸化物担体に少なくともアルカリ金属を含む NO_x 吸蔵材と貴金属とを担持してなる NO_x 吸蔵還元型の排ガス浄化用触媒であって、 NO_x 吸蔵材は、アルカリ金属からなる核体と核体の周囲を覆

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うシェル層とからなるコア・シェル構造をもち、シェル層はアルカリ土類金属、希土類元素、Mn、Fe、Co、及びNiから選ばれる元素を含むことにある。

【0013】

【発明の実施の形態】本発明の排ガス浄化用触媒では、アルカリ金属からなる核体と核体の周囲を覆うシェル層とからなる、コア・シェル構造のNO_x吸蔵材を担持している。シェル層の融点はアルカリ金属より高いので、高温時にアルカリ金属よりなる核体が液状となっても固体状態のシェル層によって流動が規制され、貴金属を覆ったり担体あるいは基材に固着したりするような不具合が抑制される。したがって高温耐久後も高いNO_x吸蔵能と高いNO_x浄化率が発現され、耐久性に優れている。

【0014】コア・シェル構造の核体であるアルカリ金属は、K、Na、Cs、Li、Rb、Frのいずれも用い得るが、K、Na、Cs、Liが好ましくKが特に好ましい。

【0015】またコア・シェル構造のシェル層は、アルカリ土類金属、希土類元素、Mn、Fe、Co、及びNiから選ばれる元素を含むものであり、これらの元素の酸化物、炭酸塩などであって、400℃以上の高温時にも固体状態であるものが用いられる。中でもBa、Ca、Mgなどのアルカリ土類元素を含むことが特に望ましい。これによって低温域におけるNO_x吸蔵能が向上し、NO_x浄化活性が一層向上する。

【0016】コア・シェル構造のNO_x吸蔵材の粒径は、0.1μm以下であることが好ましく、0.05μm以下であることがさらに望ましい。粒径がこれより大きくなると表面積の低下によりNO_x吸蔵材の担持量当たりのNO_x吸蔵能が低下する。そのため多量に担持せざるを得ず、そうすると貴金属の担持量に影響が及ぶ場合がある。また核体とシェル層の比率は特に制限されないが、重量比で核体/シェル層=1/4~1/2の範囲が好ましい。

【0017】このようなコア・シェル構造のNO_x吸蔵材を製造するには種々の方法が考えられるが、例えば逆ミセルを用いる方法がある。この方法は、先ずベンゼンなどの非水溶媒に、分子中にアルカリ土類金属などを含む界面活性剤を添加して逆ミセルを形成する。そこへアルカリ金属塩の水溶液を添加すると、逆ミセルの中心の親水性部分にアルカリ金属塩の水溶液の液滴が保持されて可溶化する。これを焼成すれば、アルカリ金属を核体としアルカリ土類金属などを含むシェル層をもつコア・シェル構造のNO_x吸蔵材粒子を製造することができる。

【0018】上記製造方法においては、逆ミセルの中心部でアルカリ金属塩を非水溶性として析出させ、それを焼成することが好ましい。これによりアルカリ金属からなる核体をさらに微細化できるので、表面積の増大によりNO_x吸蔵能及びNO_x浄化能がさらに向上する。このようにアルカリ金属塩を析出させるには、例えば酒石酸水溶液を混合して逆ミセルの中心部でアルカリ金属の酒

石酸水素塩を形成する方法がある。

【0019】本発明の排ガス浄化用触媒に用いられる酸化物担体としては、Al₂O₃、TiO₂、ZrO₂、CeO₂、SiO₂、MgOなどの一種又は複数種、あるいはこれらから選ばれた複数種からなる複合酸化物などを用いることができる。そして酸化物担体粉末をペレット状に形成し、それにコア・シェル構造のNO_x吸蔵材と貴金属を担持してペレット触媒としてもよいし、コーゼライトあるいは金属箔などから形成されたハニカム基材に酸化物担体粉末からなるコート層を形成し、それにコア・シェル構造のNO_x吸蔵材と貴金属を担持してハニカム触媒とすることもできる。

【0020】酸化物担体にコア・シェル構造のNO_x吸蔵材を担持するには、酸化物担体粉末とコア・シェル構造のNO_x吸蔵材粒子からなる粉末を混合してコート層を形成することによって行うことができる。なお、コア・シェル構造のNO_x吸蔵材は、炭酸塩処理などによってシェル層を非水溶性としておくことが望ましい。これによりコート層形成時の水性スラリー中にコア・シェル構造のNO_x吸蔵材が析出するのを防止することができる。

【0021】またコア・シェル構造のNO_x吸蔵材の担持とともに、従来のNO_x吸蔵還元型触媒のようにアルカリ金属塩の水溶液をコート層に吸収させてアルカリ金属を担持することも好ましい。これにより微細なアルカリ金属塩を担持できるので、初期のNO_x浄化活性を向上させることができる。ただそのアルカリ金属が高温時に移動して貴金属を覆ったりするのを低減するために、微細なアルカリ金属の担持量は極く少量とすべきである。

【0022】コア・シェル構造のNO_x吸蔵材の担持量は、アルカリ金属として触媒1リットルあたり0.01~2モルとなるようにすることが好ましい。NO_x吸蔵材の担持量がこれより少ないとNO_x吸蔵能及びNO_x浄化率が実用的でなく、これより多くなると貴金属の担持量が相対的に減少するため活性が低下する。

【0023】また本発明の排ガス浄化用触媒にいう貴金属としては、Pt、Rh、Pd、Ir、Ruなどから選ばれる一種又は複数種を用いることができる。この貴金属の担持量は触媒1リットルあたり0.5~20重量%とするのが好ましい。これより少ないと実用的な活性が発現されず、これより多く担持しても活性が飽和するとともに高価となる。貴金属の担持方法は従来と同様に行うことができ、吸着担持法あるいは含浸担持法でコート層に担持すればよい。

【0024】

【実施例】以下、実施例及び比較例により本発明を具体的に説明する。

【0025】(実施例1)図1に本発明の一実施例の触媒の拡大説明図を示す。この触媒は、Al₂O₃、TiO₂及びZrO₂よりなる担体1と、担体1に担持されたコア・シェル構造のNO_x吸蔵材2と、担体1に担持されたPt3とから

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ら構成されている。コア・シェル構造の NO_x 吸蔵材2は、 $\text{K}(\text{K}_2\text{O})$ よりなる核体20と、核体20の表面に形成され $\text{Ca}(\text{Ca}(\text{O}_3)_2)$ よりなるシェル層21とから構成されている。以下、図2を参照しながらこの触媒の製造方法を説明して、構成の詳細な説明に代える。

【0026】ベンゼン 341gに 1,2ビス(2エチルヘキシル)スルホコハク酸カルシウム $([(\text{C}_2\text{OH}_{37}\text{O}_4)\text{SO}_4]_2 \cdot \text{Ca}^{2+})$ の1モルを加え、攪拌し完全に溶解してベンゼン溶液Aを調製した。これにより 1,2ビス(2エチルヘキシル)スルホコハク酸カルシウムは、親水基を内側に疎水基を外側に向けて会合し逆ミセルを形成する。

【0027】一方、純水に炭酸カリウムを加え攪拌して完全に溶解し、濃度45~52重量%の炭酸カリウム水溶液Bを調製した。そしてベンゼンと水の重量比がベンゼン/水=3.5となるように、ベンゼン溶液A全量を攪拌しながら炭酸カリウム水溶液Bを加えて溶液Cを調製した。逆ミセルの中心部は親水性が強いので、炭酸カリウム水溶液Bの液滴が逆ミセルの中心部に存在した状態で可溶化される。

【0028】他方、ベンゼン 325gに 1,2ビス(2エチルヘキシル)スルホコハク酸カルシウム0.95モルを加え、攪拌し完全に溶解してベンゼン溶液Dを調製した。これにより逆ミセルが形成される。一方、純水に酒石酸を加え攪拌して完全に溶解し、濃度50~58重量%の酒石酸水溶液Eを調製した。そしてベンゼンと水の重量比がベンゼン/水=3.5となるように、ベンゼン溶液D全量を攪拌しながら酒石酸水溶液Eを加えて溶液Fを調製した。逆ミセルの中心部は親水性が強いので、酒石酸水溶液Eの液滴が逆ミセルの中心部に存在した状態で可溶化される。

【0029】次に溶液Cを攪拌しながら溶液Fの全量を加え、1時間攪拌を続行した。これにより逆ミセルの中心で炭酸カリウム水溶液Bと酒石酸水溶液Eが混合され、逆ミセルの中心部に水への溶解度が小さい酒石酸水素カリウムが析出する。

【0030】その後ロータリエバポレータを用いて溶媒を除去し、 O_2 を1%含む N_2 ガス雰囲気下にて550℃で2時間焼成して、コア・シェル構造の粒子の集合体である粉末を調製した。このコア・シェル構造の粒子は、 K_2O からなる核体と、 CaO からなるシェル層とから構成されている。得られた粉末を所定濃度の炭酸水素アンモニウム水溶液に浸漬して処理し、シェル層を水に不溶の炭酸塩 $(\text{Ca}(\text{CO}_3)_2)$ としてコア・シェル構造の NO_x 吸蔵材粉末を調製した。

【0031】 Al_2O_3 粉末 100重量部と、 TiO_2 粉末 100重量部と、 ZrO_2 粉末50重量部と、上記 NO_x 吸蔵材粉末6重量部を混合し、適量のアルミナゾルと純水を加えてスラリーを調製した。そしてコーゼライト製のハニカム基材(直径100mm、長さ163mm、セル密度400/in²)を用いて、このスラリーをウォッシュコートした後、250

℃で60分間乾燥し、450℃で2時間焼成してコート層を形成した。コート層はハニカム基材1リットルあたりに250g形成され、ハニカム基材1リットルあたりにKが0.1モル、Caが0.5モル担持されている。

【0032】上記コート層が形成されたハニカム基材に所定濃度のジニトロジアミン白金水溶液の所定量を含浸し、蒸発乾燥後、450℃で2時間焼成してPtを担持した。Ptの担持量は、ハニカム基材1リットルあたり2gである。

【0033】(実施例2) 1,2ビス(2エチルヘキシル)スルホコハク酸カルシウムに代えて 1,2ビス(2エチルヘキシル)スルホコハク酸マグネシウム $([(\text{C}_2\text{OH}_{37}\text{O}_4)\text{SO}_4]_2 \cdot \text{Mg}^{2+})$ を同量用いたこと以外は実施例1と同様にしてコア・シェル構造の NO_x 吸蔵材粉末を調製し、同様にコート層を形成しPtを担持して実施例2の触媒とした。

【0034】(実施例3) ベンゼン 341gに 1,2ビス(2エチルヘキシル)スルホコハク酸カルシウムの1モルを加え、攪拌し完全に溶解してベンゼン溶液Aを調製した。これにより 1,2ビス(2エチルヘキシル)スルホコハク酸カルシウムは、親水基を内側に疎水基を外側に向けて会合し逆ミセルを形成する。

【0035】一方、純水に炭酸ナトリウム10水和物を加え攪拌して完全に溶解し、濃度70~80重量%の炭酸ナトリウム水溶液Gを調製した。そしてベンゼンと水の重量比がベンゼン/水=3.5となるように、ベンゼン溶液Aの全量を攪拌しながら炭酸ナトリウム水溶液Gを加えて溶液Hを調製した。逆ミセルの中心部は親水性が強いので、炭酸ナトリウム水溶液Gの液滴が逆ミセルの中心部に存在した状態で可溶化される。

【0036】次に溶液Hに CO_2 ガスをバブリングしながら1時間攪拌し、逆ミセルを水に難溶の炭酸塩 $(\text{Ca}(\text{CO}_3)_2)$ とした。その後ロータリエバポレータを用いて溶媒を除去し、 O_2 を1%含む N_2 ガス雰囲気下にて550℃で2時間焼成して、コア・シェル構造の粒子の集合体である NO_x 吸蔵材粉末を調製した。この NO_x 吸蔵材粉末は、 Na_2O からなる核体と、 $\text{Ca}(\text{CO}_3)_2$ からなるシェル層とから構成されている。

【0037】この NO_x 吸蔵材粉末を用いたこと以外は実施例1と同様にしてコート層を形成し、Ptを担持して実施例3の触媒とした。

【0038】(実施例4) 1,2ビス(2エチルヘキシル)スルホコハク酸カルシウムに代えて 1,2ビス(2エチルヘキシル)スルホコハク酸マグネシウムを同量用いたこと以外は実施例3と同様にしてコア・シェル構造の NO_x 吸蔵材粉末を調製し、同様にコート層を形成しPtを担持して実施例4の触媒とした。

【0039】(比較例1) Al_2O_3 粉末 100重量部と、 TiO_2 粉末 100重量部と、 ZrO_2 粉末50重量部を混合し、適量のアルミナゾルと純水を加えてスラリーを調製した。そ

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して実施例1と同様のハニカム基材を用意し、このスラリーをウォッシュコートした後、250°Cで60分間乾燥し、450°Cで2時間焼成してコート層を形成した。コート層はハニカム基材1リットルあたりに250g形成された。

【0040】次に上記コート層が形成されたハニカム基材に所定濃度のジニトロジアミン白金水溶液の所定量を含浸し、蒸発乾固後、450°Cで2時間焼成してPtを担持した。Ptの担持量は、ハニカム基材1リットルあたり2gである。

【0041】そしてPtが担持されたコート層をもつハニカム基材に、所定量の硝酸カリウムと硝酸カルシウムを溶解した混合水溶液の所定量を含浸し、蒸発乾固後、450°Cで2時間焼成してKとCaを担持した。Kの担持量は、ハニカム基材1リットルあたり0.1モルであり、Caの担持量は、ハニカム基材1リットルあたり0.5モルである。

【0042】(比較例2) 比較例1と同様に形成されたPtが担持されたコート層をもつハニカム基材を用い、硝

酸カルシウム水溶液に代えて硝酸マグネシウム水溶液を用いたこと以外は比較例1と同様にしてKとCaを同量担持した。

【0043】(比較例3) 比較例1と同様に形成されたPtが担持されたコート層をもつハニカム基材を用い、硝酸カリウム水溶液に代えて硝酸ナトリウム水溶液を用いたこと以外は比較例1と同様にしてNaとCaを同量担持した。

【0044】(比較例3) 比較例1と同様に形成されたPtが担持されたコート層をもつハニカム基材を用い、硝酸カリウム水溶液に代えて硝酸ナトリウム水溶液を用いたこと、硝酸カルシウム水溶液に代えて硝酸マグネシウム水溶液を用いたこと以外は比較例1と同様にしてNaとMgを同量担持した。

【0045】<試験・評価>各実施例及び各比較例の触媒の構成を表1に示す。

【0046】

【表1】

実施例	担体	核体 (担持量)	シェル層 (担持量)	貴金属 (担持量)
実施例1		K (0.1mol/L)	Ca (0.5mol/L)	Pt (2g/L)
実施例2		K (0.1mol/L)	Mg (0.5mol/L)	
実施例3		Na (0.1mol/L)	Ca (0.5mol/L)	
実施例4	Al ₂ O ₃ +TiO ₂ +ZrO ₂	Na (0.1mol/L)	Mg (0.5mol/L)	
比較例1	(100) (100) (50)	K (0.1mol/L)+Ca (0.5mol/L)		
比較例2		K (0.1mol/L)+Mg (0.5mol/L)		
比較例3		Na (0.1mol/L)+Ca (0.5mol/L)		
比較例4		Na (0.1mol/L)+Mg (0.5mol/L)		

【0047】各実施例及び各比較例の触媒を排気量1800ccのリ・ンバーンエンジンの排気系にそれぞれ搭載し、9Lapモードで50時間運転する耐久試験を行った。耐久試験の際の触媒床温度の最大値は800°Cである。

【0048】そして耐久試験後に、A/F=22相当のリ・ンガス1分間とA/F=12相当のリッチガス1秒間の繰り返し昇降気下におけるNO_x浄化率を種々の触媒床温度でそれぞれ測定し、結果を図3に示す。

【0049】図3より各実施例の触媒は対応する各比較例の触媒に比べて、250～480°Cの各触媒床温度で高いNO_x浄化率を示していることがわかる。これはコア・シェル構造のNO_x吸蔵材を担持した効果であることが明らかであり、主に耐久試験時にKの移動によってPtが覆われるのが抑制された効果であると考えられる。

【0050】

【発明の効果】本発明の排ガス浄化用触媒によれば、アルカリ金属の移動が抑制され、NO_x浄化能の耐久性が向上する。

【図面の簡単な説明】

【図1】本発明の一実施例の触媒の構成を示す説明図である。

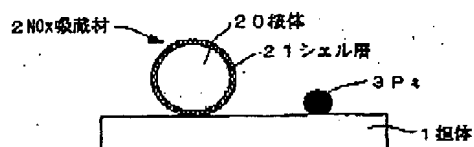
【図2】本発明の一実施例におけるコア・シェル構造のNO_x吸蔵材の製造方法を示す説明図である。

【図3】実施例及び比較例の触媒の触媒床温とNO_x浄化率の関係を示すグラフである。

【符号の説明】

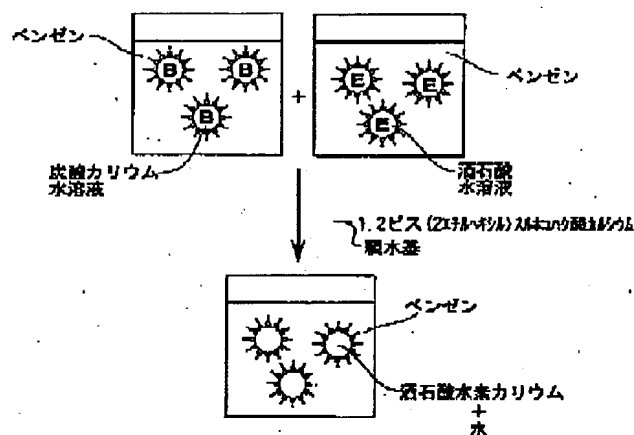
1：担体 2：NO_x吸蔵材 3：Pt
20：核体 21：シェル層

【図1】

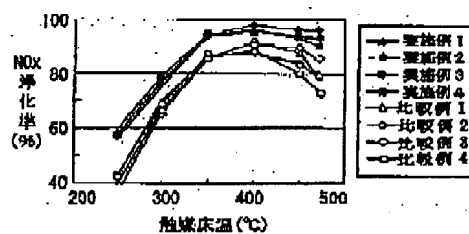


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【図2】



【図3】



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フロントページの続き

Fターム(参考) 3G09I AA12 AB06 BA07 BA14 BA39
FB10 FB12 GA06 GB01X
GB01Y GB02Y GB03Y GB04Y
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BA03X BA06Y BA07X BA08X
BA14X BA15X BA16Y BA26Y
BA30X BA31Y BA32Y BA33Y
BA36Y BA37Y BA38Y BA41Y
BA42X BA45X BB02 BB16
EA04
4G069 AA03 AA08 BA01A BA01B
BA02A BA04A BA04B BA05A
BA05B BA13A BB02A BB02B
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BC07A BC08A BC09B BC10B
BC38A BC43A BC62A BC66A
DC67A BC68A DC69A DC70A
BC71A BC72A BC74A BC75A
DC75B CA03 CA08 CA13
EA18 EC28 EC29 EE01 FA01
FB05 FC10

2003-117399 TOYOTA MOTOR CORP**EXHAUST GAS CLEANING CATALYST****Abstract:**

PROBLEM TO BE SOLVED: To suppress the migration of an alkali metal and to enhance the permanence of NOx removing power.

SOLUTION: An NOx occluding material has a core-shell structure comprising a core body comprising an alkali metal and a shell layer coating the periphery of the core body, wherein the shell layer contains an element selected from the alkaline earth metals, the rare earth elements, Mn, Fe, Co and Ni. Since the shell layer is in the solid state at high temperature, the migration of the alkali metal is regulated by the shell layer.

CLAIMS**[Claim(s)]**

[Claim 1] NOx which contains alkali metal in oxide support at least NOx which comes to support occlusion material and noble metals It is the catalyst for emission gas purification of an occlusion reduction type, and is this NOx. It is the catalyst for emission gas purification which occlusion material has the core shell structure which consists of a wrap shell layer the perimeter of a nuclide and this nuclide which consists of alkali metal, and is characterized by this shell layer containing alkaline earth metal, rare earth elements, and an element chosen from Mn, Fe, Co, and nickel.

DETAILED DESCRIPTION**[Detailed Description of the Invention]****[0001]**

[The technical field to which invention belongs] This invention is NOx at the lean atmosphere of hyperoxia. NOx by which carried out occlusion and occlusion was carried out in the rich ambient atmosphere where a reduction component is superfluous NOx which can be emitted and returned It is related with the catalyst for emission gas purification of an occlusion reduction type.

[0002]

[Description of the Prior Art] In recent years, the global warming by the carbon dioxide poses a problem, and it has been a technical problem to reduce the discharge of a carbon dioxide. Also in an automobile, reduction of the amount of carbon dioxides in exhaust gas serves as a technical problem, and the lean burn engine to which lean combustion of the fuel is carried out in a hyperoxia ambient atmosphere is developed. Since the amount of the fuel used is reduced according to this lean burn engine, the discharge of a carbon dioxide can be controlled.

[0003] It is NO_x, making it always burn on the fuel Lean conditions of hyperoxia in this lean burn engine, and using exhaust gas as reducing atmosphere by considering as fuel SUTOIKI - rich conditions intermittently. The system which carries out reduction clarification is developed and put in practical use. And as the optimal catalyst for this system, it is NO_x at lean atmosphere. NO_x by which occlusion was carried out by carrying out occlusion NO_x emitted in SUTOIKI or a rich ambient atmosphere NO_x using occlusion material. The catalyst for emission gas purification of an occlusion reduction type is developed.

[0004] For example, the catalyst for emission gas purification which supported alkaline earth metal and Pt(s), such as Ba, to porosity oxide support, such as gamma-aluminum 2O₃, is proposed by JP,5-317652,A. Moreover, publication number The catalyst for emission gas purification which supported alkali metal and Pt(s), such as K, to porosity oxide support, such as gamma-aluminum 2O₃, is proposed by 6 No. -31139 official report. Furthermore, the catalyst for emission gas purification which supported rare earth elements and Pt(s), such as La, to porosity oxide support, such as gamma-aluminum 2O₃, is proposed by JP,5-168860,A. Alkali metal, alkaline earth metal, and rare earth elements are NO_x. Since it has the property which carries out occlusion bleedoff, it is NO_x. It is called occlusion material.

[0005] This NO_x If an occlusion reduction type catalyst is used, exhaust gas will also consist pulse-like of lean atmosphere with SUTOIKI or a rich ambient atmosphere by controlling an air-fuel ratio to consist pulse-like of a Lean side SUTOIKI or a rich side. Therefore, at the Lean side, it is NO_x. NO_x It is NO_x even if it is exhaust gas from a lean burn engine, since occlusion is carried out to occlusion material, it is emitted by SUTOIKI or the rich side, it reacts with reducibility components, such as HC and CO, and it is purified. It can purify efficiently. Moreover, HC and CO in exhaust gas are NO_x while oxidizing with noble metals. Since it is consumed by reduction, HC and CO are also purified efficiently.

[0006] NO_x With an occlusion reduction type catalyst, NO in exhaust gas oxidizes by the catalysis of noble metals in the lean atmosphere of hyperoxia, and it is NO₂. It becomes, it serves as nitrite ion or nitrate ion with a steam, and it is NO_x. It reacts with occlusion material and occlusion is carried out. Therefore, noble metals and NO_x It is desirable to approach mutually and to be supported and occlusion material is NO_x by this. Occlusion ability is discovered by max and it is high NO_x. The rate of clarification is discovered.

[0007] On the other hand, it is NO_x. The alkali metal as occlusion material is NO_x in a pyrosphere. NO_x used in the exhaust gas of an elevated temperature in recent years since it excels in occlusion ability. It is an indispensable component at the occlusion reduction type catalyst. Therefore, NO_x For an occlusion reduction type catalyst, noble metals and alkali metal are indispensable, and it is desirable for it to approach mutually moreover and to be supported.

[0008] However, generally the melting point is low, it moves in a support top at the time of an elevated temperature, the activity of noble metals falls a noble-metals front face by the bonnet and this, and alkali metal is NO_x. There was nonconformity that occlusion

ability fell. For example, a potassium is K_2O . The melting point in the condition The melting point in the condition of K (NO_3) which is 402 degrees C and carried out occlusion of the NO_x It becomes 337 degrees C. The sake it will liquefy at the exhaust gas temperature of about 400 degrees C, a support top will be flowed, and noble metals will be covered.

[0009] Then, although separating into a respectively different support particle, and supporting noble metals and alkali metal, or separating them in a support layer is performed, it compares, when approaching and supporting, and it is NO_x . Occlusion ability falls and it is NO_x . There is a problem that the rate of clarification also falls. Moreover, it is NO_x , if there is also alkali metal which dissolves to base materials, such as alkali metal which disperses at the time of an elevated temperature, and porosity oxide support or cordierite, and it becomes such. Occlusion ability falls and it is NO_x like activity lowering of noble metals. The rate of clarification will fall.

[0010] Therefore, although it is most desirable to prevent migration of the alkali metal at the time of an elevated temperature, the actual condition is that the effective cure is not found out from the situation of the own property of alkali metal.

[0011]

[Problem(s) to be Solved by the Invention] It is made in view of such a situation, migration of alkali metal is controlled, and this invention is NO_x . It aims at considering as the catalyst which raised the endurance of decontamination capacity.

[0012]

[Means for Solving the Problem] The feature of a catalyst for emission gas purification of this invention which solves the above-mentioned technical problem is NO_x which contains alkali metal in oxide support at least. NO_x which comes to support occlusion material and noble metals It is the catalyst for emission gas purification of an occlusion reduction type, and is NO_x . Occlusion material has the core shell structure which consists of a wrap shell layer the perimeter of a nuclide and a nuclide which consists of alkali metal, and a shell layer is to include alkaline earth metal, rare earth elements, and an element chosen from Mn, Fe, Co, and nickel.

[0013]

[Embodiment of the Invention] NO_x of the core shell structure which consists of a wrap shell layer the perimeter of a nuclide and a nuclide which consists of alkali metal with the catalyst for emission gas purification of this invention Occlusion material is supported. Since the melting point of a shell layer is higher than alkali metal, even if the nuclide which consists of alkali metal at the time of an elevated temperature becomes liquefied, floating is regulated by the shell layer of a solid state and nonconformity which covers noble metals or dissolves to support or a base material is controlled. Therefore, NO_x even with after [high] elevated-temperature durability Occlusion ability and high NO_x The rate of clarification is discovered and it excels in endurance.

[0014] Although both K, Na, Cs Li Rb and Fr can be used for the alkali metal which is the nuclide of a core shell structure, K, Na, Cs, and Li are desirable and especially its K is

especially desirable.

[0015] moreover, the shell layers of a core shell structure are the oxide of these elements, a carbonate, etc. including alkaline earth metal, rare earth elements, and the element chosen from Mn, Fe, Co, and nickel -- what is a solid state is used also at the time of the elevated temperature of 400 or more degrees C. Especially the thing included for alkaline earth elements, such as Ba, calcium, and Mg, especially is desirable. NOx [in / by this / a low-temperature region] Occlusion ability improves and it is NOx. Clarification activity improves further.

[0016] NOx of a core shell structure It is desirable that they are the particle size of occlusion material and 0.1 micrometers or less, and it is still more desirable that it is 0.05 micrometers or less. If particle size becomes larger than this, it is NOx by lowering of surface area. NOx per amount of support of occlusion material Occlusion ability falls. therefore, a large quantity -- not supporting -- if it does not obtain but becomes so, effect may attain to the amount of support of noble metals Moreover, although especially the ratio of a nuclide and a shell layer is not restricted, the range of a nuclide / shell layer = 1 / 4 - 1/2 is desirable at a weight ratio.

[0017] NOx of such a core shell structure Although various methods can be considered to manufacture occlusion material, there is a method using reversed micelle, for example. First, into a molecule, this method adds the surfactant containing alkaline earth metal etc., and forms reversed micelle at non-aqueous solvents, such as benzene. If the aqueous solution of an alkali-metal salt is added there, into the hydrophilic portion of the center of reversed micelle, the drop of the aqueous solution of an alkali-metal salt will be held, and it will solubilize. NOx of a core shell structure with the shell layer which makes alkali metal a nuclide and contains alkaline earth metal etc. if this is calcinated An occlusion material particle can be manufactured.

[0018] In the above-mentioned manufacture method, it is desirable to deposit an alkali-metal salt as nonaqueous solubility in the core of reversed micelle, and to calcinate it. The nuclide which consists of alkali metal by this can be made still more detailed, and it is NOx of a core shell structure. Since-izing of the occlusion material can be carried out [detailed], it is NOx by buildup of surface area. Occlusion ability and NOx Decontamination capacity improves further. Thus, in order to deposit an alkali-metal salt, there is the method of mixing a tartaric-acid aqueous solution and forming the bitartrate of alkali metal in the core of reversed micelle.

[0019] as the oxide support used for the catalyst for emission gas purification of this invention -- aluminum 2O3, and TiO2, ZrO2, CeO2, SiO2 and MgO etc. -- the multiple oxide which consists of a kind, two or more sorts, or two or more sorts that were chosen from these can be used. And oxide support powder is formed in a pellet type, and it is NOx of a core shell structure to it. Occlusion material and noble metals are supported, it is good also as a pellet catalyst, the coat layer which becomes the honeycomb base material formed from cordierite or a metallic foil from oxide support powder is formed, and it is NOx of a core shell structure to it. Occlusion material and noble metals can be

supported and it can also consider as a honeycomb catalyst.

[0020] It is NOx of a core shell structure to oxide support. In order to support occlusion material, it is NOx of oxide support powder and a core shell structure. It can carry out by mixing the powder which consists of an occlusion material particle, and forming a coat layer. In addition, NOx of a core shell structure As for occlusion material, what the shell layer is made into nonaqueous solubility for by carbonatization processing etc. is desirable. Thereby, it is NOx of a core shell structure in the aqueous slurry at the time of the coat stratification. It can prevent that occlusion material is eluted.

[0021] Moreover, NOx of a core shell structure In support of occlusion material, it is the conventional NOx. It is also desirable to make the aqueous solution of an alkali-metal salt absorb water in a coat layer like an occlusion reduction type catalyst, and to support alkali metal. Since a detailed alkali metal can be supported by this, it is early NOx. Clarification activity can be raised. In order to reduce the alkali metal merely moving at the time of an elevated temperature, and covering noble metals, the amount of support of a detailed alkali metal should be made **** small quantity.

[0022] NOx of a core shell structure As for the amount of support of occlusion material, it is desirable to make it become 0.01-2 mols per 1l. of catalysts as an alkali metal. NOx It is NOx if there are few amounts of support of occlusion material than this. Occlusion ability and NOx If the rate of clarification is not practical and increases more than this, in order that the amount of support of noble metals may decrease relatively, activity falls.

[0023] Moreover, as noble metals said to the catalyst for emission gas purification of this invention, a kind chosen from Pt, Rh, Pd, Ir, Ru, etc. or two or more sorts can be used. The amount of support of these noble metals is per 1l. of catalysts. It is desirable to consider as 0.5 - 20 % of the weight. It becomes expensive, while activity will be saturated even if practical activity is not discovered but it supports mostly from this if fewer than this. What is necessary is to be able to perform the support method of noble metals as usual, and just to support it with the adsorption supporting method or the impregnation supporting method in a coat layer.

[0024]

[Example] Hereafter, an example and the example of a comparison explain this invention concretely.

[0025] (Example 1) Amplification explanatory drawing of the catalyst of one example of this invention is shown in drawing 1. NOx of the core shell structure supported by this catalyst, aluminum 2O3, the support 1 that consists of TiO2 and ZrO2, and support 1 It consists of occlusion material 2 and Pt3 supported by support 1. NOx of a core shell structure The occlusion material 2 consists of a nuclide 20 which consists of K (K2O), and a shell layer 21 which is formed in the front face of a nuclide 20 and consists of calcium (calcium2 (CO3)). The manufacture method of this catalyst is explained hereafter, referring to drawing 2, and it replaces with detailed explanation of a

configuration.

[0026] Benzene To 341g One mol of 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium ($[(C_2OH_3CO_2)SO_4]^{2-}$ and calcium $^{2+}$) was added and agitated, it dissolved thoroughly, and the benzene solution A was prepared. Thereby A hydrophilic group is turned inside, they turn a hydrophobic group outside, and 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium meet, and form reversed micelle.

[0027] On the other hand, potassium carbonate was added and agitated to pure water, it dissolved in it thoroughly, and the potassium carbonate aqueous solution B of 45 - 52 % of the weight of concentration was prepared. And agitating the benzene solution A whole quantity so that the weight ratio of benzene and water may be set to benzene / water = 3.5, the potassium carbonate aqueous solution B was added and Solution C was prepared. Since the core of reversed micelle has strong hydrophilicity, after the drop of the potassium carbonate aqueous solution B has existed in the core of reversed micelle, it is solubilized.

[0028] On the other hand, benzene To 325g 1 and 0.95 mols of 2 screw (2 ethylhexyl) sulfo succinic-acid calcium were added and agitated, it dissolved thoroughly, and the benzene solution D was prepared. Thereby, reversed micelle is formed. On the other hand, the tartaric acid was added and agitated to pure water, it dissolved in it thoroughly, and the tartaric-acid aqueous solution E of 50 - 58 % of the weight of concentration was prepared. And agitating the benzene solution D whole quantity so that the weight ratio of benzene and water may be set to benzene / water = 3.5, the tartaric-acid aqueous solution E was added and Solution F was prepared. Since the core of reversed micelle has strong hydrophilicity, after the drop of the tartaric-acid aqueous solution E has existed in the core of reversed micelle, it is solubilized.

[0029] Next, the whole quantity of Solution F was added agitating Solution C, and churning was continued for 1 hour. The potassium carbonate aqueous solution B and the tartaric-acid aqueous solution E are mixed by this at the center of reversed micelle, and a potassium hydrogen tartrate with the small solubility to water deposits in the core of reversed micelle.

[0030] Under N₂ gas ambient atmosphere which removes a solvent using a rotary evaporator after that, and contains O₂ 1% It calcinated at 550 degrees C for 2 hours, and the powder which is the aggregate of the particle of a core shell structure was prepared. It consists of a particle of this core shell structure, a nuclide which consists of K₂O, and a shell layer which consists of CaO. It is immersed in the ammonium-hydrogencarbonate aqueous solution of predetermined concentration, the obtained powder is processed, and it is NO_x of a core shell structure considering a shell layer as a carbonate (calcium $^{2+}$ (CO₃)) insoluble in water. Occlusion material powder was prepared.

[0031] 2Oaluminum₃ powder The 100 weight sections and TiO₂ powder The 100 weight sections, the ZrO₂ powder 50 weight section, and Above NO_x The occlusion material powder 66 weight section was mixed, the alumina sol and pure water of optimum dose were added, and the slurry was prepared. And it dries for 60 minutes at 250 degree C

after preparing the honeycomb base material made from cordierite (diameter 100mm, length 163mm and cel density 400-/in²) and carrying out the wash coat of this slurry. It calcinated at 450 degrees C for 2 hours, and the coat layer was formed. A coat layer is per 1l. of honeycomb base materials. 250g is formed and it is K to per 1l. of honeycomb base materials. 0.1 mols and calcium 0.5 mols are supported.

[0032] The specified quantity of the dinitro diamine platinum aqueous solution of predetermined concentration was sunk into the honeycomb base material with which the above-mentioned coat layer was formed, it calcinated at the evaporation-to-dryness back and 450 degree C for 2 hours, and Pt was supported. The amount of support of Pt is 2g per 1l. of honeycomb base materials.

[0033] (Example 2) 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium -- replacing with -- Except is made to be the same as that of an example 1. 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid magnesium ([(C₂OH 37O₄) SO₄-] 2andMg²⁺) -- **** for tales doses -- things -- NO_x of a core shell structure Occlusion material powder was prepared, the coat layer was formed similarly, Pt was supported, and it considered as the catalyst of an example 2.

[0034] (Example 3) Benzene To 341g One mol of 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium was added and agitated, it dissolved thoroughly, and the benzene solution A was prepared. Thereby A hydrophilic group is turned inside, they turn a hydrophobic group outside, and 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium meet, and form reversed micelle.

[0035] On the other hand, sodium-carbonate 10 hydrate was added and agitated to pure water, it dissolved in it thoroughly, and the sodium-carbonate aqueous solution G of 70 - 80 % of the weight of concentration was prepared. And agitating the whole quantity of the benzene solution A so that the weight ratio of benzene and water may be set to benzene / water = 3.5, the sodium-carbonate aqueous solution G was added and Solution H was prepared. Since the core of reversed micelle has strong hydrophilicity, after the drop of the sodium-carbonate aqueous solution G has existed in the core of reversed micelle, it is solubilized.

[0036] In next, the solution H It agitated for 1 hour, carrying out bubbling of the CO₂ gas, and reversed micelle was used as the refractory carbonate (calcium₂ (CO₃)) at water. Under N₂ gas ambient atmosphere which removes a solvent using a rotary evaporator after that, and contains O₂ 1% NO_x which it calcinates at 550 degrees C for 2 hours, and is the aggregate of the particle of a core shell structure Occlusion material powder was prepared. This NO_x Occlusion material powder consists of a nuclide which consists of Na₂O, and a shell layer which consists of calcium (CO₃)₂.

[0037] This NO_x Except having used occlusion material powder, the coat layer was formed like the example 1, Pt was supported, and it considered as the catalyst of an example 3.

[0038] (Example 4) 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium -- replacing with -- 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid magnesium -- **** for tales doses -- things -- except -- an example 3 -- the same -- carrying out -- NOx of a core shell structure Occlusion material powder was prepared, the coat layer was formed similarly, Pt was supported, and it considered as the catalyst of an example 4.

[0039] (Example 1 of a comparison) 2Oaluminum3 powder The 100 weight sections and TiO2 powder The 100 weight sections and the ZrO2 powder 50 weight section were mixed, the alumina sol and pure water of optimum dose were added, and the slurry was prepared. And it dries for 60 minutes at 250 degcc C after preparing the same honeycomb base material as an example 1 and carrying out the wash coat of this slurry. It calcinated at 450 degrees C for 2 hours, and the coat layer was formed. A coat layer is per 1l. of honeycomb base materials. 250g was formed.

[0040] Next, the specified quantity of the dinitro diamine platinum aqueous solution of predetermined concentration was sunk into the honeycomb base material with which the above-mentioned coat layer was formed, it calcinated at the evaporation-to-dryness back and 450 degree C for 2 hours, and Pt was supported. The amount of support of Pt is 2g per 1l. of honeycomb base materials.

[0041] And it sank in, the specified quantity of the mixed aqueous solution which the potassium nitrate and calcium nitrate of the specified quantity dissolved in the honeycomb base material with the coat layer with which Pt was supported was calcinated at the evaporation-to-dryness back and 450 degree C for 2 hours, and K and calcium were supported. The amount of support of K is per 1l. of honeycomb base materials. It is 0.1 mols and the amount of support of calcium is per 1l. of honeycomb base materials. It is 0.5 mols.

[0042] (Example 2 of a comparison) Tales-doses support of K and Mg was carried out like the example 1 of a comparison except having replaced with the calcium nitrate aqueous solution and having used the magnesium nitrate aqueous solution using the honeycomb base material with the coat layer with which Pt formed like the example 1 of a comparison was supported.

[0043] (Example 3 of a comparison) Tales-doses support of Na and the calcium was carried out like the example 1 of a comparison except having replaced with the potassium-nitrate aqueous solution and having used the sodium-nitrate aqueous solution using the honeycomb base material with the coat layer with which Pt formed like the example 1 of a comparison was supported.

[0044] (Example 3 of a comparison) Tales-doses support of Na and Mg was carried out like the example 1 of a comparison except having replaced with the potassium-nitrate aqueous solution and having used the sodium-nitrate aqueous solution using the honeycomb base material with the coat layer with which Pt formed like the example 1 of a comparison was supported, and having replaced with the calcium nitrate aqueous solution and having used the magnesium nitrate aqueous solution.

[0045] The configuration of the catalyst of <trial / assessment> each example and each example of a comparison is shown in a table 1.

[0046]

[A table 1]

[0047] The catalyst of each example and each example of a comparison was carried in the exhaust air system of a lean burn engine with a displacement of 1800 cc, respectively, and the durability test operated in 9Lap mode for 50 hours was performed. Maximum of whenever [catalyst floor temperature / in the case of a durability test] It is 800 degrees C.

[0048] And for [equivalent to $A/F=22$ after durability test lean gas] 1 minute NO_x under the repeat ambient atmosphere for [equivalent to $A/F=12$ rich gas] 1 second The rate of clarification is measured by whenever [various catalyst floor temperature], respectively, and a result is shown in drawing 3.

[0049] the catalyst of each example is compared with the corresponding catalyst of each example of a comparison from drawing 3 -- NO_x high whenever [each catalyst floor temperature / of 250 to 480 degree C] It turns out that the rate of clarification is shown. This is NO_x of a core shell structure. It is thought that it is clear that it is the effect which supported occlusion material, and that Pt is mainly covered with migration of K at the time of a durability test is the controlled effect.

[0050]

[Effect of the Invention] According to the catalyst for emission gas purification of this invention, migration of alkali metal is controlled, and it is NO_x . The endurance of decontamination capacity improves.

TECHNICAL FIELD

[A technical field to which invention belongs] This invention is NO_x at lean atmosphere of hyperoxia. NO_x by which carried out occlusion and occlusion was carried out in a rich ambient atmosphere where a reduction component is superfluous NO_x which can be emitted and returned It is related with a catalyst for emission gas purification of an occlusion reduction type.

PRIOR ART

[Description of the Prior Art] In recent years, the global warming by the carbon dioxide poses a problem, and it has been a technical problem to reduce the discharge of a carbon dioxide. Also in an automobile, reduction of the amount of carbon dioxides in exhaust gas serves as a technical problem, and the lean burn engine to which lean combustion of the fuel is carried out in a hyperoxia ambient atmosphere is developed. Since the amount of the fuel used is reduced according to this lean burn engine, the discharge of a carbon dioxide can be controlled.

[0003] It is NOx, making it always burn on the fuel Lean conditions of hyperoxia in this lean burn engine, and using exhaust gas as reducing atmosphere by considering as fuel SUTOIKI - rich conditions intermittently. The system which carries out reduction clarification is developed and put in practical use. And as the optimal catalyst for this system, it is NOx at lean atmosphere. NOx by which occlusion was carried out by carrying out occlusion NOx emitted in SUTOIKI or a rich ambient atmosphere NOx using occlusion material. The catalyst for emission gas purification of an occlusion reduction type is developed.

[0004] For example, the catalyst for emission gas purification which supported alkaline earth metal and Pt(s), such as Ba, to porosity oxide support, such as gamma-aluminum 2O3, is proposed by JP,5-317652,A. Moreover, publication number The catalyst for emission gas purification which supported alkali metal and Pt(s), such as K, to porosity oxide support, such as gamma-aluminum 2O3, is proposed by 6 No. -31139 official report. Furthermore, the catalyst for emission gas purification which supported rare earth elements and Pt(s), such as La, to porosity oxide support, such as gamma-aluminum 2O3, is proposed by JP,5-168860,A. Alkali metal, alkaline earth metal, and rare earth elements are NOx. Since it has the property which carries out occlusion bleedoff, it is NOx. It is called occlusion material.

[0005] This NOx If an occlusion reduction type catalyst is used, exhaust gas will also consist pulse-like of lean atmosphere with SUTOIKI or a rich ambient atmosphere by controlling an air-fuel ratio to consist pulse-like of a Lean side SUTOIKI or a rich side. Therefore, at the Lean side, it is NOx. NOx It is NOx even if it is exhaust gas from a lean burn engine, since occlusion is carried out to occlusion material, it is emitted by SUTOIKI or the rich side, it reacts with reducibility components, such as HC and CO, and it is purified. It can purify efficiently. Moreover, HC and CO in exhaust gas are NOx while oxidizing with noble metals. Since it is consumed by reduction, HC and CO are also purified efficiently.

[0006] NOx With an occlusion reduction type catalyst, NO in exhaust gas oxidizes by the catalysis of noble metals in the lean atmosphere of hyperoxia, and it is NO2. It becomes, it serves as nitrite ion or nitrate ion with a steam, and it is NOx. It reacts with occlusion material and occlusion is carried out. Therefore, noble metals and NOx It is desirable to approach mutually and to be supported and occlusion material is NOx by this. Occlusion

ability is discovered by max and it is high NOx. The rate of clarification is discovered.

[0007] On the other hand, it is NOx. The alkali metal as occlusion material is NOx in a pyrosphere. NOx used in the exhaust gas of an elevated temperature in recent years since it excels in occlusion ability. It is an indispensable component at the occlusion reduction type catalyst. Therefore, NOx. For an occlusion reduction type catalyst, noble metals and alkali metal are indispensable, and it is desirable for it to approach mutually moreover and to be supported.

[0008] However, generally the melting point is low, it moves in a support top at the time of an elevated temperature, the activity of noble metals falls a noble-metals front face by the bonnet and this, and alkali metal is NOx. There was nonconformity that occlusion ability fell. For example, a potassium is K2O. The melting point in the condition The melting point in the condition of K (NO3) which is 402 degrees C and carried out occlusion of the NOx. It becomes 337 degrees C. The sake It will liquefy at the exhaust gas temperature of about 400 degrees C, a support top will be flowed, and noble metals will be covered.

[0009] Then, although separating into a respectively different support particle, and supporting noble metals and alkali metal, or separating them in a support layer is performed, it compares, when approaching and supporting, and it is NOx. Occlusion ability falls and it is NOx. There is a problem that the rate of clarification also falls. Moreover, it is NOx, if there is also alkali metal which dissolves to base materials, such as alkali metal which disperses at the time of an elevated temperature, and porosity oxide support or cordierite, and it becomes such. Occlusion ability falls and it is NOx like activity lowering of noble metals. The rate of clarification will fall.

[0010] Therefore, although it is most desirable to prevent migration of the alkali metal at the time of an elevated temperature, the actual condition is that the effective cure is not found out from the situation of the own property of alkali metal.

EFFECT OF THE INVENTION

[Effect of the Invention] According to the catalyst for emission gas purification of this invention, migration of alkali metal is controlled, and it is NOx. The endurance of decontamination capacity improves.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] It is made in view of such a situation, migration of alkali metal is controlled, and this invention is NOx. It aims at considering as the catalyst which raised the endurance of decontamination capacity.

MEANS

[Means for Solving the Problem] The feature of a catalyst for emission gas purification of this invention which solves the above-mentioned technical problem is NO_x which contains alkali metal in oxide support at least. NO_x which comes to support occlusion material and noble metals. It is the catalyst for emission gas purification of an occlusion reduction type, and is NO_x. Occlusion material has the core shell structure which consists of a wrap shell layer the perimeter of a nuclide and a nuclide which consists of alkali metal, and a shell layer is to include alkaline earth metal, rare earth elements, and an element chosen from Mn, Fe, Co, and nickel.

[0013]

[Embodiment of the Invention] NO_x of the core shell structure which consists of a wrap shell layer the perimeter of a nuclide and a nuclide which consists of alkali metal with the catalyst for emission gas purification of this invention. Occlusion material is supported. Since the melting point of a shell layer is higher than alkali metal, even if the nuclide which consists of alkali metal at the time of an elevated temperature becomes liquefied, floating is regulated by the shell layer of a solid state and nonconformity which covers noble metals or dissolves to support or a base material is controlled. Therefore, NO_x even with after [high] elevated-temperature durability. Occlusion ability and high NO_x. The rate of clarification is discovered and it excels in endurance.

[0014] Although both K, Na, Cs, Li, Rb and Fr can be used for the alkali metal which is the nuclide of a core shell structure, K, Na, Cs, and Li are desirable and especially K is desirable.

[0015] moreover, the shell layers of a core shell structure are the oxide of these elements, a carbonate, etc. including alkaline earth metal, rare earth elements, and the element chosen from Mn, Fe, Co, and Ni -- what is a solid state is used also at the time of the elevated temperature of 400 or more degrees C. Especially the thing included for alkaline earth elements, such as Ba, calcium, and Mg, especially is desirable. NO_x [in / by this / a low-temperature region] Occlusion ability improves and it is NO_x. Clarification activity improves further.

[0016] NO_x of a core shell structure. It is desirable that they are the particle size of occlusion material and 0.1 micrometers or less, and it is still more desirable that it is 0.05 micrometers or less. If particle size becomes larger than this, it is NO_x by lowering of surface area. NO_x per amount of support of occlusion material. Occlusion ability falls. therefore, a large quantity -- not supporting -- if it does not obtain but becomes so, effect may attain to the amount of support of noble metals. Moreover, although especially the ratio of a nuclide and a shell layer is not restricted, the range of a nuclide / shell layer = 1 / 4 - 1/2 is desirable at a weight ratio.

[0017] NO_x of such a core shell structure. Although various methods can be considered to manufacture occlusion material, there is a method using reversed micelle, for example. First, into a molecule, this method adds the surfactant containing alkaline earth metal etc.,

and forms reversed micelle at non-aqueous solvents, such as benzene. If the aqueous solution of an alkali-metal salt is added there, into the hydrophilic portion of the center of reversed micelle, the drop of the aqueous solution of an alkali-metal salt will be held, and it will solubilize. NOx of a core shell structure with the shell layer which makes alkali metal a nuclide and contains alkaline earth metal etc. if this is calcinated An occlusion material particle can be manufactured.

[0018] In the above-mentioned manufacture method, it is desirable to deposit an alkali-metal salt as nonaqueous solubility in the core of reversed micelle, and to calcinate it. The nuclide which consists of alkali metal by this can be made still more detailed, and it is NOx of a core shell structure. Since-izing of the occlusion material can be carried out [detailed], it is NOx by buildup of surface area. Occlusion ability and NOx Decontamination capacity improves further. Thus, in order to deposit an alkali-metal salt, there is the method of mixing a tartaric-acid aqueous solution and forming the bitartrate of alkali metal in the core of reversed micelle.

[0019] as the oxide support used for the catalyst for emission gas purification of this invention -- aluminum $2O_3$, and TiO_2 , ZrO_2 , CeO_2 , SiO_2 and MgO etc. -- the multiple oxide which consists of a kind, two or more sorts, or two or more sorts that were chosen from these can be used. And oxide support powder is formed in a pellet type, and it is NOx of a core shell structure to it. Occlusion material and noble metals are supported, it is good also as a pellet catalyst, the coat layer which becomes the honeycomb base material formed from cordierite or a metallic foil from oxide support powder is formed, and it is NOx of a core shell structure to it. Occlusion material and noble metals can be supported and it can also consider as a honeycomb catalyst.

[0020] It is NOx of a core shell structure to oxide support. In order to support occlusion material, it is NOx of oxide support powder and a core shell structure. It can carry out by mixing the powder which consists of an occlusion material particle, and forming a coat layer. In addition, NOx of a core shell structure As for occlusion material, what the shell layer is made into nonaqueous solubility for by carbonatization processing etc. is desirable. Thereby, it is NOx of a core shell structure in the aqueous slurry at the time of the coat stratification. It can prevent that occlusion material is eluted.

[0021] Moreover, NOx of a core shell structure In support of occlusion material, it is the conventional NOx. It is also desirable to make the aqueous solution of an alkali-metal salt absorb water in a coat layer like an occlusion reduction type catalyst, and to support alkali metal. Since a detailed alkali metal can be supported by this, it is early NOx. Clarification activity can be raised. In order to reduce the alkali metal merely moving at the time of an elevated temperature, and covering noble metals, the amount of support of a detailed alkali metal should be made **** small quantity.

[0022] NOx of a core shell structure As for the amount of support of occlusion material, it is desirable to make it become 0.01-2 mols per 1l. of catalysts as an alkali metal. NOx It is NOx if there are few amounts of support of occlusion material than this. Occlusion ability and NOx If the rate of clarification is not practical and increases more than this, in

order that the amount of support of noble metals may decrease relatively, activity falls.

[0023] Moreover, as noble metals said to the catalyst for emission gas purification of this invention, a kind chosen from Pt, Rh, Pd, Ir, Ru, etc. or two or more sorts can be used. The amount of support of these noble metals is per 11. of catalysts. It is desirable to consider as 0.5 - 20 % of the weight. It becomes expensive, while activity will be saturated even if practical activity is not discovered but it supports mostly from this if fewer than this. What is necessary is to be able to perform the support method of noble metals as usual, and just to support it with the adsorption supporting method or the impregnation supporting method in a coat layer.

EXAMPLE

[Example] Hereafter, an example and the example of a comparison explain this invention concretely.

[0025] (Example 1) Amplification explanatory drawing of the catalyst of one example of this invention is shown in drawing 1. NOx of the core shell structure supported by this catalyst, aluminum 2O3, the support 1 that consists of TiO2 and ZrO2, and support 1 It consists of occlusion material 2 and Pt3 supported by support 1. NOx of a core shell structure The occlusion material 2 consists of a nuclide 20 which consists of K (K2O), and a shell layer 21 which is formed in the front face of a nuclide 20 and consists of calcium (calcium2 (CO3)). The manufacture method of this catalyst is explained hereafter, referring to drawing 2, and it replaces with detailed explanation of a configuration.

[0026] Benzene To 341g One mol of 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium $[(C_2OH\ 37O_4)\ SO_4-]\ 2andcalcium^{2+}$ was added and agitated, it dissolved thoroughly, and the benzene solution A was prepared. Thereby A hydrophilic group is turned inside, they turn a hydrophobic group outside, and 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium meet, and form reversed micelle.

[0027] On the other hand, potassium carbonate was added and agitated to pure water, it dissolved in it thoroughly, and the potassium carbonate aqueous solution B of 45 - 52 % of the weight of concentration was prepared. And agitating the benzene solution A whole quantity so that the weight ratio of benzene and water may be set to benzene / water = 3.5, the potassium carbonate aqueous solution B was added and Solution C was prepared. Since the core of reversed micelle has strong hydrophilicity, after the drop of the potassium carbonate aqueous solution B has existed in the core of reversed micelle, it is solubilized.

[0028] On the other hand, benzene To 325g 1 and 0.95 mols of 2 screw (2 ethylhexyl) sulfo succinic-acid calcium were added and agitated, it dissolved thoroughly, and the benzene solution D was prepared. Thereby, reversed micelle is formed. On the other hand, the tartaric acid was added and agitated to pure water, it dissolved in it thoroughly,

and the tartaric-acid aqueous solution E of 50 - 58 % of the weight of concentration was prepared. And agitating the benzene solution D whole quantity so that the weight ratio of benzene and water may be set to benzene / water = 3.5, the tartaric-acid aqueous solution E was added and Solution F was prepared. Since the core of reversed micelle has strong hydrophilicity, after the drop of the tartaric-acid aqueous solution E has existed in the core of reversed micelle, it is solubilized.

[0029] Next, the whole quantity of Solution F was added agitating Solution C, and churning was continued for 1 hour. The potassium carbonate aqueous solution B and the tartaric-acid aqueous solution E are mixed by this at the center of reversed micelle, and a potassium hydrogen tartrate with the small solubility to water deposits in the core of reversed micelle.

[0030] Under N₂ gas ambient atmosphere which removes a solvent using a rotary evaporator after that, and contains O₂ 1% It calcinated at 550 degrees C for 2 hours, and the powder which is the aggregate of the particle of a core shell structure was prepared. It consists of a particle of this core shell structure, a nuclide which consists of K₂O, and a shell layer which consists of CaO. It is immersed in the ammonium-hydrogencarbonate aqueous solution of predetermined concentration, the obtained powder is processed, and it is NO_x of a core shell structure considering a shell layer as a carbonate (calcium₂ (CO₃)) insoluble in water. Occlusion material powder was prepared.

[0031] 2Oaluminum₃ powder The 100 weight sections and TiO₂ powder The 100 weight sections, the ZrO₂ powder 50 weight section, and Above NO_x The occlusion material powder 66 weight section was mixed, the alumina sol and pure water of optimum dose were added, and the slurry was prepared. And it dries for 60 minutes at 250 degree C after preparing the honeycomb base material made from cordierite (diameter 100mm, length 163mm and cel density 400-/in²) and carrying out the wash coat of this slurry. It calcinated at 450 degrees C for 2 hours, and the coat layer was formed. A coat layer is per 1l. of honeycomb base materials. 250g is formed and it is K to per 1l. of honeycomb base materials. 0.1 mols and calcium 0.5 mols are supported.

[0032] The specified quantity of the dinitro diamine platinum aqueous solution of predetermined concentration was sunk into the honeycomb base material with which the above-mentioned coat layer was formed, it calcinated at the evaporation-to-dryness back and 450 degree C for 2 hours, and Pt was supported. The amount of support of Pt is 2g per 1l. of honeycomb base materials.

[0033] (Example 2) 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium -- replacing with -- Except is made to be the same as that of an example 1. 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid magnesium ([C₂OH 37O₄] SO₄-] 2andMg²⁺) -- **** for tales doses -- things -- NO_x of a core shell structure Occlusion material powder was prepared, the coat layer was formed similarly, Pt was supported, and it considered as the catalyst of an example 2.

[0034] (Example 3) Benzene To 341g One mol of 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium was added and agitated, it dissolved thoroughly, and the benzene

solution A was prepared. Thereby A hydrophilic group is turned inside, they turn a hydrophobic group outside, and 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium meet, and form reversed micelle.

[0035] On the other hand, sodium-carbonate 10 hydrate was added and agitated to pure water, it dissolved in it thoroughly, and the sodium-carbonate aqueous solution G of 70 - 80 % of the weight of concentration was prepared. And agitating the whole quantity of the benzene solution A so that the weight ratio of benzene and water may be set to benzene / water = 3.5, the sodium-carbonate aqueous solution G was added and Solution H was prepared. Since the core of reversed micelle has strong hydrophilicity, after the drop of the sodium-carbonate aqueous solution G has existed in the core of reversed micelle, it is solubilized.

[0036] In next, the solution H It agitated for 1 hour, carrying out bubbling of the CO₂ gas, and reversed micelle was used as the refractory carbonate (calcium₂ (CO₃)) at water. Under N₂ gas ambient atmosphere which removes a solvent using a rotary evaporator after that, and contains O₂ 1% NO_x which it calcinates at 550 degrees C for 2 hours, and is the aggregate of the particle of a core shell structure Occlusion material powder was prepared. This NO_x Occlusion material powder consists of a nuclide which consists of Na₂O, and a shell layer which consists of calcium (CO₃)₂.

[0037] This NO_x Except having used occlusion material powder, the coat layer was formed like the example 1, Pt was supported, and it considered as the catalyst of an example 3.

[0038] (Example 4) 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid calcium -- replacing with -- 1 and 2 screw (2 ethylhexyl) sulfo succinic-acid magnesium -- **** for tales doses -- things -- except -- an example 3 -- the same -- carrying out -- NO_x of a core shell structure Occlusion material powder was prepared, the coat layer was formed similarly, Pt was supported, and it considered as the catalyst of an example 4.

[0039] (Example 1 of a comparison) Al₂O₃ powder The 100 weight sections and TiO₂ powder The 100 weight sections and the ZrO₂ powder 50 weight section were mixed, the alumina sol and pure water of optimum dose were added, and the slurry was prepared. And it dries for 60 minutes at 250 degree C after preparing the same honeycomb base material as an example 1 and carrying out the wash coat of this slurry. It calcinated at 450 degrees C for 2 hours, and the coat layer was formed. A coat layer is per 1l. of honeycomb base materials. 250g was formed.

[0040] Next, the specified quantity of the dinitro diamine platinum aqueous solution of predetermined concentration was sunk into the honeycomb base material with which the above-mentioned coat layer was formed, it calcinated at the evaporation-to-dryness back and 450 degree C for 2 hours, and Pt was supported. The amount of support of Pt is 2g per 1l. of honeycomb base materials.

[0041] And it sank in, the specified quantity of the mixed aqueous solution which the potassium nitrate and calcium nitrate of the specified quantity dissolved in the honeycomb base material with the coat layer with which Pt was supported was calcinated at the evaporation-to-dryness back and 450 degree C for 2 hours, and K and calcium were supported. The amount of support of K is per 1l. of honeycomb base materials. It is 0.1 mols and the amount of support of calcium is per 1l. of honeycomb base materials. It is 0.5 mols.

[0042] (Example 2 of a comparison) Tales-doses support of K and Mg was carried out like the example 1 of a comparison except having replaced with the calcium nitrate aqueous solution and having used the magnesium nitrate aqueous solution using the honeycomb base material with the coat layer with which Pt formed like the example 1 of a comparison was supported.

[0043] (Example 3 of a comparison) Tales-doses support of Na and the calcium was carried out like the example 1 of a comparison except having replaced with the potassium-nitrate aqueous solution and having used the sodium-nitrate aqueous solution using the honeycomb base material with the coat layer with which Pt formed like the example 1 of a comparison was supported.

[0044] (Example 3 of a comparison) Tales-doses support of Na and Mg was carried out like the example 1 of a comparison except having replaced with the potassium-nitrate aqueous solution and having used the sodium-nitrate aqueous solution using the honeycomb base material with the coat layer with which Pt formed like the example 1 of a comparison was supported, and having replaced with the calcium nitrate aqueous solution and having used the magnesium nitrate aqueous solution.

[0045] The configuration of the catalyst of <trial / assessment> each example and each example of a comparison is shown in a table 1.

[0046]
[A table 1]

[0047] The catalyst of each example and each example of a comparison was carried in the exhaust air system of a lean burn engine with a displacement of 1800 cc, respectively, and the durability test operated in 9Lap mode for 50 hours was performed. Maximum of whenever [catalyst floor temperature / in the case of a durability test] It is 800 degrees C.

[0048] And for [equivalent to A/F=22 after durability test lean gas] 1 minute NOx under the repeat ambient atmosphere for [equivalent to A/F=12 rich gas] 1 second The rate of clarification is measured by whenever [various catalyst floor temperature], respectively, and a result is shown in drawing 3 .

[0049] the catalyst of each example is compared with the corresponding catalyst of each example of a comparison from drawing 3 -- NOx high whenever [each catalyst floor temperature / of 250 to 480 degree C] It turns out that the rate of clarification is shown. This is NOx of a core shell structure. It is thought that it is clear that it is the effect which supported occlusion material, and that Pt is mainly covered with migration of K at the time of a durability test is the controlled effect.

[0050]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is explanatory drawing showing the configuration of the catalyst of one example of this invention.

[Drawing 2] NOx of the core shell structure in one example of this invention It is explanatory drawing showing the manufacture method of occlusion material.

[Drawing 3] The catalyst floor temperature and NOx of a catalyst of an example and the example of a comparison It is the graph which shows the relation of the rate of clarification.

[Description of Notations]

1: Support 2:NOx Occlusion material 3 :P t

20: Nuclide 21: Shell layer

